

ENERGETIC SYSTEMS AND NANOTECHNOLOGY - A LOOK AHEAD

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ABSTRACT

Amongst the military services, the Navy has taken a unique approach to developing energetic systems over the years, primarily due to the fact that our sailors “sleep on their munitions”. While constantly striving for more powerful and effective energetic systems, there is corresponding emphasis, as well, on making sure these systems are insensitive to unplanned stimuli and do not operate until desired. Hence, the desire for “sixth generation energetic systems” incorporating the features noted above, whether employed in propellants or munitions. This paper will address two topics: 1) How nano-based materials can contribute to revolutionary improvements in energetic materials including a paradigm shift in insensitive munitions built around the idea of “Combat Safe” Insensitive Munitions (CSIM); and 2) the importance of developing the next generation of in-house experts in energetic systems who will carry on a tradition of transitioning breakthrough research into military systems.

SIXTH GENERATION ENERGETIC SYSTEMS

It can be reasonably argued that there are few systems within the U.S. Department of Defense (DoD) that require a higher degree of reliability than those incorporating energetic materials. Amongst the military services, the Navy has taken a unique approach to developing energetic systems over the years, primarily due to the fact that our sailors “sleep on their munitions”. While constantly striving for more powerful and effective energetic systems, there is a corresponding emphasis as well on making sure these systems are insensitive to unplanned stimuli and do not operate until desired. In addition to those seemingly contradictory requirements there has been of late great pressure to reduce the development time for new systems, including those with energetic materials, to be deployed into the fleet.¹⁻⁵

Key Words: Navy, nanoscience, nanotechnology, energetic materials, energetics experts

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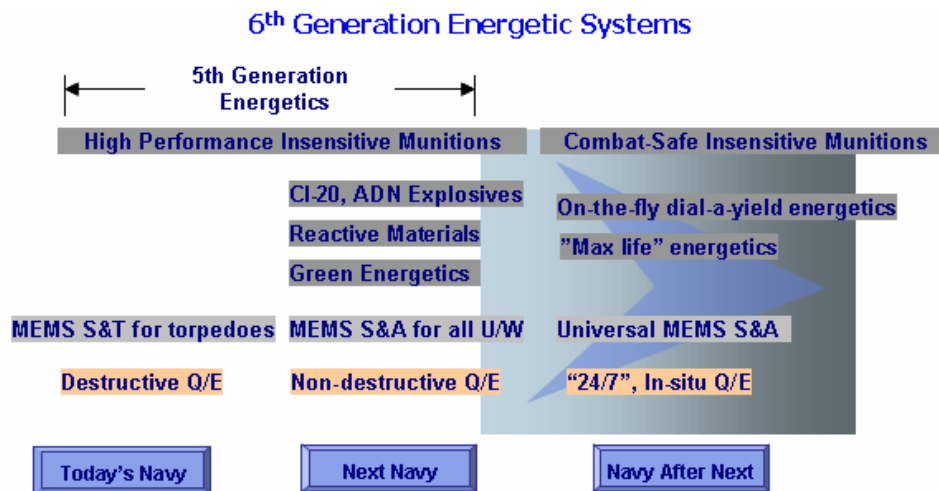


Figure 1. Sixth generation energetic systems

In 2001 the leadership of the Naval Undersea Warfare Center commissioned a study to create a vision for the "Navy After Next" in mission areas critical to Undersea Warfare. As part of that study, Kavetsky and Doherty coined the term "sixth generation energetic systems" as a way to depict future applications for certain naval systems. That terminology is based on the transition in energetic materials from the ancient black powder, through generations of materials based on nitrocellulose and nitroglycerin, simple TNT-based explosives, nitramine-dominated melt-cast explosives, and plastic bonded explosives (PBXs), to the use of non-traditional combinations of materials to provide large amounts of energy in a very short time. Each new generation offered some improvements over the previous ones in performance, processability, safety, or a combination of these features. Figure 1 captures portions of that forward-looking vision for the application of new and advanced energetic materials for Naval applications.

The Navy has a long and distinguished history of developing just such new and more powerful, yet insensitive munitions. In the 1990s, 12 new energetic materials developed by the Navy were transitioned into 43 weapons systems within the DoD. It is the view of many in the S&T community that nano-based energetics will be a key enabler of advances in military systems in the next 30 years.

Several research initiatives are under way between the Indian Head Division, Naval Surface Warfare Center (IHDIV/NSWC), the University of Maryland at College Park (UMCP), and the U.S. Naval Academy (USNA) to look at ways to incorporate nano-scale approaches that will enable more capable energetic systems, and introduce them into use in a more timely fashion. Nanostructured materials can play a significant role in developing a new class of energetic materials with controlled and tailored energy release.

One approach to increasing performance is to place the metal fuel and nitramine material in much closer proximity to each other than can be realized by traditional formulation, which should enhance the metal oxidation reaction. A key aspect of that approach is to develop methods to vapor deposit nitramines onto combustible metal surfaces. In order to be able to perform compositional analysis and in-situ characterization using x-ray photoelectron and infrared reflection-absorption spectroscopy and temperature programmed desorption, it was necessary to develop a specialized Ultra-high Vacuum (UHV) apparatus, which is shown in Figure 2. This has been successfully created⁶ and is being used to prepare RDX-coated nano aluminum and aluminum-coated RDX using the vapor deposition process (RDX, also called cyclonite, is a white crystalline solid energetic material).



Figure 2. UHV apparatus for in-situ surface analysis of vapor deposited nitramines.

A second approach to improving material performance is to look at the possibility of surface functionalization of aluminum particles using self-assembled monolayers (SAMs). The hope is that this formulation of SAM on metal particles will protect the surface of the underlying metal from oxidation by ambient oxygen. Depending on the nature of the molecules used to form the monolayer, some additional energy content may be introduced into the coated materials. Figure 3 depicts the process suggested. The unpassivated metal nanoparticles are prepared and passivated using SAMs. The coating may be performed on metals with or without a thin oxide coating on the surface. In either case, a functional group reacts with the surface of the nanoparticles to form a chemical bond between the atoms or molecules on the surface of the particle and the functional group, in this case a carboxylic acid group, in the coating material. SAM/unpassivated aluminum has been successfully prepared, and plans for formulating sample materials for combustion and detonation experiments are under way.⁷

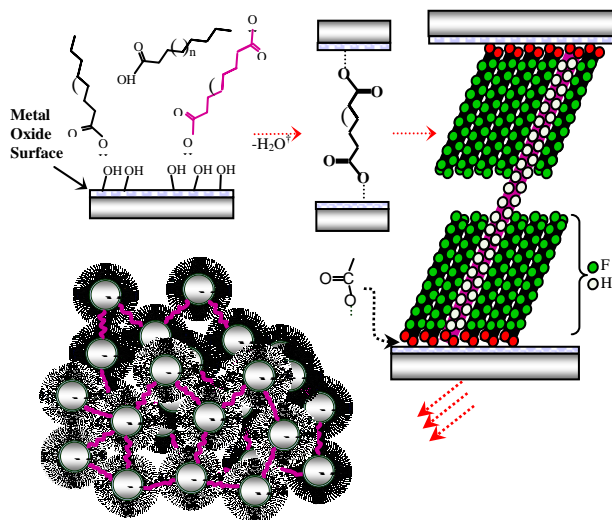


Figure 3. In the case of unpassivated Al, H₂ is released during the coating step, and a covalent Al-O-C bond forms.

Combat-Safe Insensitive Munitions

Historically, the Navy has improved the insensitivity of materials primarily through chemistry approaches, looking at new molecules and crystals, novel binders, and suppression agents. In 2004 a paradigm shift occurred with the advent of “Combat Safe Insensitive Munitions”, a concept that stresses a platform-based approach to insensitivity rather than exclusively a materials-based approach. Increased importance is placed on mechanics-based approaches to increasing insensitivity by improvements in crystal quality and crystal size, more rigorously quantifying sensitivity, and developing novel scale-up and manufacturing approaches. Figure 4 captures this philosophy concisely. The goal of this change in approach is to develop weapons capable of surviving sympathetic detonation by providing class 1.6 (non-mass detonating) materials in all future weapons.

In collaborative activities between IHDIV/NSWC, UMCP and USNA are participating in a unique experiment, wherein development of new energetic materials and the methods to produce them take place concurrently. This approach has been cultivated in large measure due to the increasing demand for shorter development timelines for new systems. In the past, it was not unusual for a new material to take 30 years to move from the lab to a fielded system. However, that time scale is no longer acceptable, as there is great pressure to reduce the development timeline for introduction of new materials.

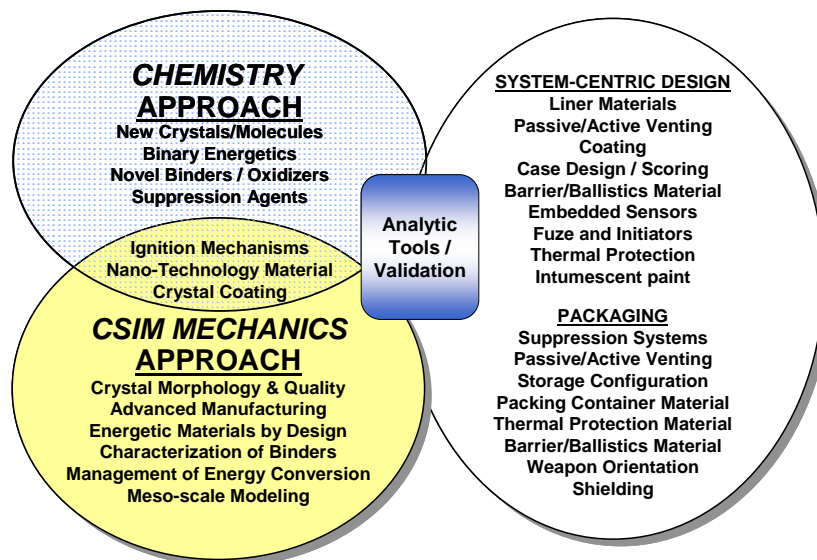


Figure 4. New Approach to Developing Combat-Safe Insensitive Munitions

UMCP, IHDIV/NSWC, and USNA are investigating advanced material concepts that are based on the multiscale structure of natural materials such as bone.⁸ The hierarchical nature of these natural materials gives them unique, defect-free structures that can exhibit multifunctional behavior. By manipulating nanostructures, such as nanoparticles and nanotubes, in macroscale processes such as Twin Screw Extrusion (TSE), bioinspired hierarchical composites are now being developed. These structures possess milliscale geometric features with mesoscale material gradients in multiple directions containing distributions of microscale and nanoscale structures. The resulting mechanical properties exhibited by these hierarchical composites are enhanced compared to their homogeneous microscale counterparts.

One specific example of such a material arises from the desire for solid rocket motors that can exhibit more than one burning rate in flight. Conventional solid rocket motors consist of a uniform propellant composition throughout the rocket motor grain. In order to provide the motor designer with new design options, the idea of using a Functionally Graded Material (FGM) with continuously varying properties along the length as well as across the radius of the grain is being explored.

Figure 5(a) depicts a stream of material leaving the TSE. Due to the flexibilities this processing approach offers, one can change the rate of different feed materials, as well as other processing variables, to achieve a desired material end-state. Figure 5(b) is a strand of material produced in the TSE with material properties being varied along the length, as the color change in the material depicts. 5(c) is a cross-sectional view of this strand of material, and 5(d) shows the grain structure of the end product.

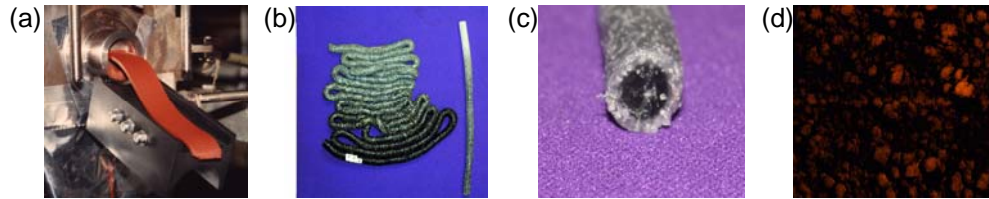


Figure 5. FGM material produced in TSE process.

Computational process and performance models are now being developed to predict the microstructural evolution of these bioinspired composites and their associated functionality in order to optimize their design for various commercial and military applications, including biomedical devices, energetic systems, and vibration control mechanisms. In fact, it is now possible in some cases to reverse engineer solid rocket motors starting with desired performance characteristics, and working back to the material configuration required for such performance. Figure 6 depicts one such design trade available to the motor designer. It is not hard to imagine how the design space could be further enlarged by taking advantage of FGMs to realize new performance. A key enabler for the FGM-based propellants is the ability to use nanoscale particles as an option in the mixing process.³

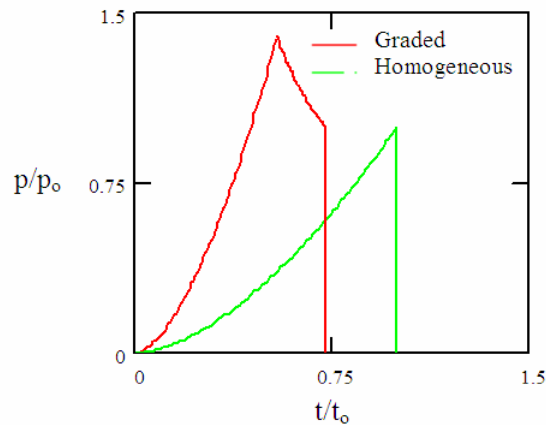


Figure 6. Design parameter flexibility enabled by FGM approach to solid rocket motor design.

Building the Intellectual Capital for the Future

Through the years the DoD has been able to provide its forces with superior warfare capabilities with their innovative use of human resources in specialized fields

such as energetic systems. Significant advances in warfare capability were brought about in large part by successful transformations introduced through the enterprise of science and technology (S&T). DoD must continue to adapt to the current pace of technological change, rapidly integrate new and breakthrough technologies into its operational systems, and sustain a research and development environment that fosters innovation in order to preserve our significant lead in military capability. To do this, DoD must continue to attract and retain the very best scientists and engineers in its workforce. This is especially true for those scientists and engineers working at the forefront of emerging S&T, such as those who work in the energetic systems arena, who require a unique set of technical skills in order to transition S&T to the fleet.

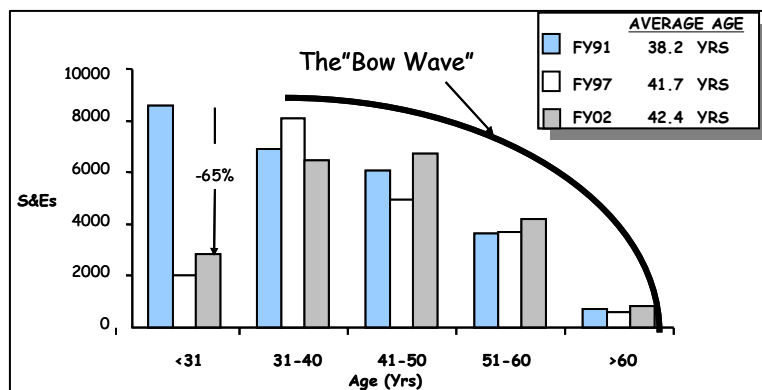


Figure 7. Demographic snapshot of the Navy's Civilian S&E Workforce

The Naval Warfare Centers

The Navy has tremendous intellectual capital in its S&T workforce, a large portion of which is resident in the Warfare Centers (WCs). Currently there are 2200 scientists and engineers (S&Es), including 850 PhDs, who work predominantly on S&T. These S&Es are unique and valuable catalysts for innovation. They must have the skills and resources to achieve the required major advances in naval warfighting effectiveness. WC research is tightly linked to warfighting capabilities and provides a critical bridge from S&T to the Fleet. Naval innovation has consistently resulted in products that significantly improve overall warfighting capability. However, the demographics of that workforce point to a trend that is cause for concern, as shown in Figure 7. Due to the reductions in hiring during the 1990s as a result of downsizing, the pipeline of new technical talent coming into the system was greatly reduced, creating the "bow-wave" effect noted. This situation is especially acute in niche areas of S&T such as energetic materials and energetic systems, where the entire population of experts is very small and highly specialized.

An additional issue is emerging which provides further emphasis to the idea that the US must have a scientifically savvy workforce. That issue is the rapid pace of

globalization of S&T as depicted in Figure 8.⁵ While the US is still a major provider of scientific discovery and engineering innovation, the rest of the world is rapidly expanding its interest and investment in S&T. The confluence of an aging workforce, the global nature of S&T, and a reduced pipeline of US citizens pursuing advanced science and engineering degrees could lead to a situation in which technological surprise is not a question of if, but when.

Thus, it is imperative that the DoD S&T enterprise focus on creating a future S&T workforce which will maintain our technological edge. One key element of that strategy is taking advantage of our current mentor-rich environment of senior scientists and engineers to train the next generation of experts, as well as to pass along the corporate technical knowledge of the S&T work performed over the past 30 years, which has resulted in our preeminent position in the world today. This is especially true in niche fields such as energetic systems, which have their primary roots in DoD-focused activities. This highlights the need for a DoD workforce of the future which is both increasingly S&T smart and connected to the global enterprise.

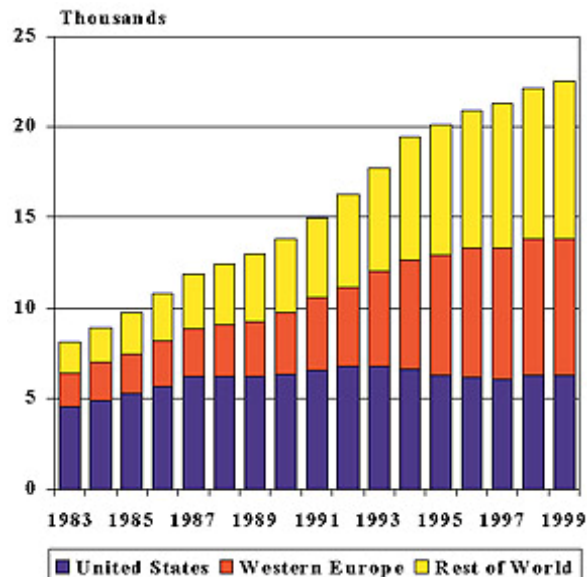


Figure 8. Total Submissions, Physical Review and Physical Review Letters

SUMMARY

The Navy views nanoscience and nanotechnology as areas of increasing importance and opportunity. The Navy's research and development organizations such as the IHDIV/NSWC provide a critical infrastructure for both performing multidisciplinary work at the nano-scale and providing critical transition paths for nanoscience and nanotechnology into a whole host of applications of interest to the Navy, such as Combat-Safe Insensitive Munitions. Academic institutions such as the

University of Maryland at College Park and the U. S. Naval Academy are conducting pioneering research work in ways to incorporate nano approaches into sixth generation energetic materials on both the material development and material production fronts, in order to realize both new capabilities and shorter development timelines. Products such as functionally graded nanocomposites are tantalizing examples of the potential for nanotechnology to bring innovations from the bench to the Fleet, while also providing an opportunity for reducing costs. In order to realize sixth generation energetic systems, a new cadre of experts needs to be grown in the Navy's R&D Centers such as IHDIV/NSWC, who can speak to both the bench scientist, as well as the development engineer responsible for transitioning S&T into the Fleet. The vision of the Navy-After-Next will only be realized if our S&T workforce is as technically competent as past generations and plugged into the global S&T network.

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